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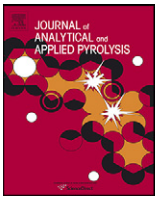

Review

Cellulose pyrolysis kinetics: An historical review on the existence and role of intermediate active cellulose

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ABSTRACT

Cellulose pyrolysis, studied since more than one century, has been the object of a great number of papers. Several related kinetic models have been established in large experimental conditions, from slow to fast pyrolysis. Unfortunately, no actual consensus is reached. The primary formation of intermediate species accompanied or not with phase change phenomena are amongst the main matters of concerns. The purpose of the present review is to report the controversies, well-established knowledges and unresolved questions concerning the existence and role of intermediate species (often called "active cellulose"). After a general discussion, a few research topics are suggested at the end of the paper.

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1. Introduction and purpose of the review

Since several millennia, biomass is considered as one of the major sources of energy, chemicals and materials as reminded by Antal and Gronli [1] in the framework of the specific case of charcoal production. The transformation of biomass can be performed either by biochemical or thermochemical routes. High temperature processes bring several advantages including the fact that all the main feedstock components (cellulose, lignin, hemicellulose) of any type of biomass can be upgraded. The great number of possible types of thermochemical processes differ according to the operating conditions, types of reactors and biomass, objectives, etc. They are usually classified into combustion, gasification and pyrolysis [2–4]. In combustion, biomass is burned under an excess of O_2 for energy generation. In gasification performed under lower O_2 fractions (or of steam) the aim is to maximise the production of gases for several possible applications: energy generation; H_2 or CH_4 preparation; production of synthetic biofuels, etc. Pyrolysis (carbonisation, distillation, pyrogasification, pyroliquefaction, slow or fast pyrolysis) is carried out under inert atmosphere with the production of various fractions of solids (charcoal), liquids (bio-oils, tars), gases. In all these thermal processes, the chemical phenomena begin with primary steps of biomass thermal decomposition followed by secondary reactions (crackings, gas phase-solid interactions, etc.). To be noticed that the same word “Pyrolysis” is used for describing either the elementary pyrolysis reactions or the whole pyrolysis process. The present paper relies on the more or less primary steps of biomass pyrolysis.

These chemical reactions are often in competition with heat and mass transfer phenomena and may also depend on the hydrodynamic characteristics of the reactor. Their relative importances depend on the experimental conditions. For example, a recent paper [4] describes the difficulties in the search of reliable criteria for defining required experimental conditions in the case of fast pyrolysis. The still bad knowledge of kinetic pathways and parameters of biomass primary pyrolysis are amongst the main difficulties. In spite of the great number (several hundred) of published papers, no consensus is presently reached in the literature. The discrepancies may result from the fact that different types of biomasses having different heterogeneous structures and properties are used. Also several published kinetic parameters may vary according to the laboratory device where they have been measured and hence, their use for modelling other operating conditions may be questioned. Other reasons include the difficulties in defining and measuring the actual biomass reaction temperature, the rapidity of chemical phenomena with resulting controls by transfer processes, etc.

Many published results have been obtained with cellulose, often considered as a model compound of biomass. Its mass fractions in biomass roughly range between 40% and 50% (on dry basis). Cellulose is a well known high molecular weight linear polymer of β-(1-4)-D-glucopyranose units linked together by (1-4)glycosidic bonds [5]. These repeating units are cellobiose units (two glucose units). Cellulose is of a crystalline nature with regions of amorphous structure. Its DP is highly variable and may reach several thousands. Groups of cellulose chains make microfibril sheets which are at the basis of complex fibres [5].

The purpose of the present paper is to review some of the main significant results published since more than 100 years in the field of cellulose thermal decomposition. Special attention is focussed on the problems connected to the existence, nature and role of intermediate species formed in the early moments of its degradation. Their formation, accompanied or not by phase change phenomena, continues to be an unresolved research topic giving rise to numerous discussions since several decades. It is not a simple academic debate. Actually, the existence and nature of such species can have more or less important impacts at different levels: interpretation of kinetic measurements, design of reactors, particles behaviours, preparation of new products, biomass combustion, fires, etc.

This review follows a chronology which is arbitrarily divided into several periods of times including:

- Brief historical considerations.
- First evidences of phase change phenomena during cellulose heating.
- First pyrolysis kinetic studies: from the 50s until the end of the 70s.
- New results published after Copper Mountain’s meeting until the end of the 80s.
- New models and controversial papers published in the 90s.
- First detailed discussion in 1999 on the existence or not of an intermediate state during biomass pyrolysis.
- Last decade (2000 until now): new results, new models, new evidences for the existence of primary intermediate species.

By the way, an other indirect purpose of the present paper is to show that interesting results have been already obtained several decades ago and that serious current interpretations should not ignore such pioneering works.

2. Brief historical considerations

2.1. Wood carbonisation and distillation

Wood thermal degradation is used by mankind since several thousand years and for a great number of applications. In his review on charcoal production, Antal and Gronli [1] report, for example, cave drawings dated 30 000–38 000 years BP and also its use for ore reduction. Greeks and Romans civilisations also extensively exploited Mediterranean forests woods for their industry (smelting works, glass making plants, etc. [6]). More quantitative works have been also published by Violette [7] in 1853 following a previous paper presented in 1851 [8] to the War Minister and Science Society Academy on the carbonisation of a great number of wood sample species. These works clearly point out the strong influence of experimental conditions on the properties of pyrolysis products. Another important work is reported in the “Traité de Métallurgie” by Gruner [9].

Wood pyrolysis liquids have been also recovered since a long time by very ancient oriental, Mediterranean and northern civilisations after separation of the charcoal out of the furnace. Their varied uses ranged, for example, from boats coatings, until corpse embalming (Egyptian Pharaons civilisation). A great number of pioneering works performed in the 18th and 19th centuries show that the liquids obtained by wood distillation contain several phases (water, "wood spirit", light oils, pyrolytic acid, tars, etc.) and a great number of unidentified chemical products.

In 1875, Gruner [9] citing also Violette works points out the influence of operating conditions on the liquids/charcoal fractions: "slowly increase of low heat intensity" produces much charcoal whilst "Intense heat rapidly applied" increases oils and tars as well as gases. In these conditions, charcoal fractions can decrease from 24–28% down to 15–18% with resulting different physical structures. Clearly the differences between slow and fast pyrolysis were already discovered. Such observations are also reported by Klar [10] who points out the effect of temperature increase rate on products yields [1].

Cited in the 1923 book of Hawley [11], Klason [12] reports works on wood distillation heated in a short time and performed under vacuum. The results are quite different as those derived from ordinary distillation: the tars fractions increase from about 10% until almost 44% and, in the same time, charcoal decreases from 30% to 10%. The tars obtained under vacuum are also different (light colour, more transparent, etc.). They exothermically decompose (into water, CO_2, tar coke and ordinary tar). The new conclusions of the authors are that vacuum conditions prevent the secondary reactions and that the exothermic character of ordinary wood distillation is not due to primary but secondary reactions. Ordinary charcoal is considered as primary charcoal plus tar coke. The notions of primary and secondary reactions, exothermic aspects of reaction and existence of several types of charcoals extensively discussed in the mid 20th century were already evidenced.

2.2. Cellulose pyrolysis

First quantitative and significant works related to the specific case of cellulose have been published between the 19th and 20th centuries.

Pictet and Sarasin [13] report in 1918 detailed studies on the thermal behaviours of both cellulose and amidon. In each case, the distillation products are different depending on whether the reaction is carried out in the presence of zinc powder or not, already showing the role of catalysts.

The same authors publish also results obtained in vacuum (12–15 mm Hg) distillation (523–623 K). They report an increase of distillate yields under fast heating. In their conditions, char yields are only 10%. Two types of distillates are obtained: 32% of an aqueous one and 44% of a yellow pastry one (to be noticed a total liquid fraction of 76%, close to current bio-oils yields). In depth studies are reported on this yellow fraction (melting point 452.5–453 K and formula $C_6H_{10}O_5$) which is attributed to levoglucosan (LVG) already discovered in 1894 by Tanret by different chemical synthesis. Sarasin assumes that LVG can be considered as an intermediate molecule during cellulose pyrolytic decomposition. The atomic structure of cellulose has been hence defined on the basis of an assumed LVG formula. The author finally points out the potential interest of cellulose pyrolysis for the industrial preparation of glucose and alcohol.

In their book "La cellulose", Clément and Rivière [14] summarise these results in 1920.

2.3. Provisional conclusions

Several results and concepts already obtained more than 100 years ago are still valid nowadays. They include:

- Rapid heating and/or operation under vacuum increase the condensable fractions.
- The concepts of biomass slow and fast pyrolysis have been already evidenced in the 19th century as well as the notions of primary and secondary reactions.
- The conditions for endo or exothermal reactions are defined.
- LVG is clearly evidenced as being the most abundant intermediate product of cellulose thermal decomposition.

3. First evidences of phase change phenomena during cellulose heating

Between the mid 60s and mid 70s three papers report works (performed out of the context of cellulose pyrolysis) evidencing phase change phenomena during cellulose heating.

In 1963, Goring [15] measure the thermal softening of various fine powders compressed in a glass capillary immersed in an oil bath heated at a given heating rate. The softening point is defined as the temperature at which the powder collapses into a solid plug. For cellulose, the softening point is not affected by the presence of moisture conversely to the cases of lignin and hemicellulose. The specific case of cellulose is interpreted as being due to its crystalline nature. According to the type of cellulose, the softening temperatures range between 504 and 526 K (526 K for Avicel cellulose). It is shown that the softening point does not seem to correspond to a straightforward glass transition nor to the melting of cellulose crystallites. In the same time, the authors notice that cellulose starts to darken with the onset of softening, accompanied with up to 35% weight loss between 528 and 538 K. It is concluded that pyrolysis would be an important factor in thermal softening.

Four years later, Back et al. [16] measure the modulus of elasticity of different papers using a nondestructive technique involving ultrasonic pulse velocity measurements in reaction times ranging from 2.5 to 3 s. The results show a glass transition temperature of the amorphous part of cellulose with an average value of about 483 K (depending on the nature of paper used). In spite of the short heating times, auto cross-linking reactions take place above about 513 K followed by thermal hardening in the 513–573 K range.

In 1974, the use of carbon dioxide laser beam allows Nordin et al. [17] to bring visual evidence of so-called molten cellulose. Heating is carried out so rapidly (heating time of 0.1 ms) that chemical reactions are minimised. It is followed by a rapid cooling in liquid nitrogen. Photographs clearly show that the initial fibrillar structure of cellulose has disappeared with formation of a few millimetres diameters bubbles, whatever the type of material. The decrease of crystallinity (65% down to 35%) index is interpreted as being not due to cellulose degradation but to the melting of the sample.

These works show that, when heated, cellulose undergoes an apparent phase change accompanied with modification of crystallinity. However, without chemical analysis, it is difficult to say if these observations correspond or not to true melting phenomena. Actually, the authors show that if heating is not fast enough cellulose decomposition is observed (pyrolysis). Nordin et al. [17] use an empirical correlation, given by Boyer [18], which is valid for a great number of polymers, between glass transition temperature (T_g) and melting temperature (T_m): $T_g = 0.7T_m$ (K). Using the above values of T_g, we can calculate a theoretical melting point of cellulose ranging between 690 and 751 K (this range of values will be later on, confirmed by several other authors).

4. First pyrolysis kinetic studies: from the 50s until the end of the 70s

The first interpretations of chemical and kinetic studies carried out with wood and its main components (including cellulose) are published during this period. Most of time, the experiments rely on mass loss measurements and in conditions of slow pyrolysis. Following the publications of Hawley [11] on wood distillation, several references can be found in the 1956 paper of Stamm [19], where chemical changes accompanying the thermal degradation of cellulose are reported. The author collects and interprets much of the results from the standpoint of reaction kinetics (for heating times ranging from minutes to several days and under temperatures from 366 until 573 K). Thermal degradation follows a first order type reaction. Activation energies (of the order of 110 kJ mol^{-1} with pre-exponential factor of 6.7×10^5 s^{-1}) for reactions giving gases and char are similar for dry wood and its major components. In the same year, Madorsky et al. [20] suggest the existence of two decomposition pathways including depolymerisation processes giving hexoses.

Pioneering experiments have been published by S. Martin in the field of the rapid thermal degradation of solids. In his 1959 paper [21], he describes an experimental analysis procedure for the analysis of non-condensable gases and condensed materials. It includes GC analysis, as well as special dynamic cold traps separating the products into several fractions and analysed by various gas solid adsorption and gas liquid partition columns. The method is applied to the case of cellulosic solids submitted to intense radiant energy. In 1965, [22] the same author reports new results on the behaviour of cellulose samples submitted to a concentrated radiation. Exposure durations range between 0.4 and 8 s. The works performed in the framework of a study of the preignition domain bring interesting results on fast pyrolysis processes. Temperature measurements associated to a related model show that ignition occurs when the surface reaction temperature reaches 873–923 K, independently of the imposed flux density (because of endothermicity of the reaction). Each test reveals that after irradiance, the remaining sample contains unreacted cellulose, char and also, poorly volatile tars (they are not recovered with condensed vapours), which are water soluble. Similar species will be evidenced much later by other authors. LVG is the main volatile product. Char fraction decreases as the flux density increases (nearly zero for the highest values).

In the same time, Lincoln [23] publishes other results of cellulose pyrolysis carried out under high radiative fluxes (refocussed carbon arc, xenon flash lamps and lasers). These results as well as those of Martin performed under short reaction times (a few seconds down to 0.5 ms) are synthesised in a paper published by Lincoln [24]. They confirm that reaction temperature would be around 873 K (independently of the flux). In addition, they confirm that, as the available flux increases, the volatiles fraction increases whilst char may decrease until zero.

From an exhaustive literature analysis and on the basis of data obtained by thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and mass spectrometric thermal analysis (MTA), Kilzer and Broido [25] propose in 1965 a general kinetic scheme for the pyrolysis of pure cellulose. Its' decomposition would occur according to two competitive reactions occurring directly from cellulose. The first one (473–553 K) is a slightly endothermic reaction of dehydration followed by an exothermal process producing char and light gaseous species. In the second one (553–613 K), cellulose is postulated to be transformed into an intermediate and unstable compound (1,4-anhydro-α-D-glucopyranose) which rearranges into LVG. The authors underline the strong influence of inorganic salts which can be explained by such a mechanism. A similar scheme has been proposed by Arsenau [26] in 1971 and by Broido and Nelson [27] in 1975. However in his review of 1995, Antal and Varhegyi [28] underline that these results have been obtained with large sample sizes favourising the possibilities of char formation through secondary vapour–solid interactions.

In 1968, Shafizadeh [29] proposes a 3 concurrent reactions scheme deduced from TGA experiments. Compared to the Kilzer and Broido [25] model, a third way is added in order to take into account the formation of gases and low molecular weight products occurring at high temperature.

During this period, the quite first moments of cellulose decomposition have been studied by different authors. The thermal depolymerisation is carried out under vaccum by Pacault and Sauret [30] between 443 and 503 K and over several hours. The reaction is followed by a viscosimetric method allowing to represent the average degree of polymerisation (DP) as a function of time. The values regularly decrease from 1360 until about 300 whatever the temperature (the asymptotic value is reached much more rapidly under high temperature – a few tens hours – than at low temperature – more than 100 h). The reaction is shown to be of zero order and to occur at the boundaries between amorphous and crystalline parts of cellulose. Chatterjee and Conrad [31] study the decomposition of cellulose by TGA between 543 and 583 K. The results show a complex behaviour up to about 40% decomposition. The reaction is considered as a two steps process (glucosidic bond scission and subsequent LVG formation). The activation energy of the initiation step is found to be 227 kJ mol^{-1} (for cotton cellulose). The pyrolytic reactions occurring between 523 and 573 K are studied in vacuum and under reaction times of up to 6 h by Halpern and Patai [32]. Amongst their different experiments, the authors determine the average DP by viscosity measurement of the nitrate. They show that whatever the temperature, the average DP (initial value of 1800) rapidly (less than 1 h) decreases down to about 200. Further diminution of the chain is slower and reaches a limited value of 160. Under these primary periods, the weight loss is small (degradation of chains is initially complete before appreciable amounts of volatiles products are formed). The DP of 200 is brought about by rapid cleavage of non-crystalline sites. In agreement with several other previous works [32,33], Golova [34] confirms that cellulose first decomposes very rapidly into low average DP (about 300 for cotton cellulose) species without appreciable mass loss (only 5%). After this short period, the DP remains constant (about 200) until up to 80% decomposition whilst the fraction of LVG increases. The first stages of cellulose decomposition mainly occur in amorphous regions. Finally the authors discuss the possible practical uses of saccharides, LVG, etc. . . .obtained by thermal degradation.

Similar results are published in the 1973 paper of Broido et al. [35] who report results of crystalline and amorphous cellulose pyrolysis performed by TGA (5 K min^{-1}). For DP determinations, the heated samples (and the controls) are nitrated and then submitted for nitrogen analysis by the ultramicro method [36]. The results show that the samples decompose into much smaller polymers lengths before any measurable mass loss. The kinetics of the DP decrease depends on cellulose type. A conclusion is that the rupture of cellulose molecules occurs at strain points (crystalline–amorphous boundaries). These findings had been previously reported by Broido and Weinstein [37].

A new kinetic model is proposed by Broido [38] from experimental results obtained by TGA under vacuum. The model includes an initial step (with high activation energy) during which cellulose initially gives rise to a compound called “active cellulose” that subsequently decomposes according to two concurrent processes giving respectively rise to volatile tars and char. In his 1995 review, Antal and Varhegyi [28] will later on discuss the other possibility of char formation through vapour–solid interactions.

A key paper is published in 1979 by Bradbury et al. [39]. Cellulose pyrolysis is performed under reduced pressure (under 15 Torr) in order to prevent secondary reactions and to improve the recovery of primary products. Actually, the authors show that char fraction increases as the pressure and sample size increase. The temperatures range from 532 K to 614 K and pyrolysis times from a few minutes until 1 h. Under the low temperature domain, the results evidence a change in the mass loss regime attributed to a high activation energy process during which cellulose passes from an inactive to an active form without sample mass loss. A new model is then proposed inside which active cellulose gives rise to two competitive first order reactions giving respectively condensable (volatiles), and char + gases fractions. The Arrehenius kinetic constants of the three processes are calculated (532–614 K):

$$k(\text{active cellulose}) = 2.8 \times 10^{19} \exp\left(-\frac{242\,000}{RT}\right) \quad (\text{s}^{-1}) \tag{1}$$

$$k(\text{vapours}) = 3.2 \times 10^{14} \exp\left(-\frac{198\,000}{RT}\right) \quad (\text{s}^{-1}) \tag{2}$$

$$k(\text{char}) = 1.3 \times 10^{10} \exp\left(-\frac{151\,000}{RT}\right) \quad (\text{s}^{-1}) \tag{3}$$

This model is traditionally called the "Broido Shafizadeh" (BS) model. It has been and continues to be very often cited and used by many authors. It has given rise to many discussions in the literature. The paper of Bradbury et al. [39] mentions the works of Shafizadeh and Bradbury [40] reporting that cellulose macromolecules are not directly converted into volatile products but undergo an initial depolymerisation leading to molecules having DP around 200. It is possible to establish a parallel between the BS model including active cellulose formation and previous observations (described above) of initial phase change phenomena and decrease of DP [15–17,30–35]. These primary partial depolymerisations reactions (before weight loss) could be at the origin of activation of cellulose. To be noticed that with such DP close to 200 and under these low temperatures conditions, these intermediate species would be probably under the form of a plastic material rather than of a true low viscosity liquid. The BS model is adopted by Shafizadeh [41] in his presentation at Copper Mountain's meeting (see below).

All these models are the most representative ones until the 80s. The papers show that the results greatly depend on operating conditions: pressure, temperature, heating rate, sample size, pretreatments, residence times, etc. According to the importance of these phenomena, the kinetic models can be more or less complex because of the existence of secondary gas phase and/or gas–solid heterogeneous reactions. A great majority of these works have been carried out under slow heating rates conditions (TGA). However, in parallel, an increasing number of authors (see for example [42]) observe that rapid biomass heating leads to different selectivities.

In October 1980, a key event has been the Specialists' Workshop on Fast Pyrolysis of Biomass" held in Copper Mountain (CO, USA). In order to represent most of literature results and on the basis of a consensus of the participants, Diebold [43] proposes a very complex and detailed chemical model. Several years after, the same author [44,45] reports a simplified model inside which the feed produces directly char competitively with the formation of active cellulose giving rise in turn to char and to a series of secondary reactions with final formation of secondary gases, vapours and tars. Amongst all the 24 communications presented at the workshop, pioneering "Hot Wire" experiments of Diebold [46] should attract attention. The author makes the demonstration that an electrically heated nichrome wire is able to "saw" through a piece of biomass as with an usual thermoplastic. Smoke is observed but no charcoal. Sawing produces a lubricated feeling during the sample pyrolysis. The microscopic observation of the pyrolysed surface allows to see the virgin biomass structure through a light coloured thin brownish tar layer (appearing as a coat of varnish). First explanation is that wood first pyrolyses to give a melted phase, which is solid at room temperature unlike usual liquid condensed vapours (as pyrolysis bio oils).

From the studies published between the 50s until the end of the 70s we can draw the following main conclusions:

- Most of pyrolysis models include two initial competing reactions giving rise to vapours (mainly LVG and char). More sophisticated models rely on 3 competing reactions.
- Former models suppose that these reactions occur directly from cellulose.
- However, several results evidence the decreases of cellulose DP (until about 200) before any weight loss. Also, low temperature experiments reveal phase changes phenomena.
- The most recent models include an initiation step prior to vapour and char formations. The most known one is the BS model. The intermediate state is called active cellulose.
- In parallel to these results obtained mainly in slow heating rate conditions first results of pyrolysis carried out under rapid heating (for example radiant heating) are published. The "Hot Wire" pyrolysis demonstration evidences the formation of liquid intermediate products.

5. New results published after Copper Mountain's meeting until the end of the 80s

Amongst the numerous papers published by M.J. Antal, several ones have been performed in the context of using concentrated radiant energy as a source of heat for fluid fuels production. Early works performed at Princeton University, in French Odeillo solar furnace as well as results obtained in bench scale facilities (artificial source of light) are gathered in a paper [47] presented at the Copper Mountain's meeting. The authors show that radiant flash pyrolysis products may be either liquid syrups or permanent gases depending upon reactor conditions. In 1982, Dejenga and Antal [48] show that LVG is a majority in the gaseous products. One year later Antal et al. [49] use the BS model for interpreting the results obtained in a continuous solar reactor. However in 1984, Hofmann and Antal [50] report results of a simulation relying on a one step mechanism. In the same year, Hopkins et al. [51] report results of cellulose flash pyrolysis carried out in a spouted bed settled at the focus of an arc image furnace (Xenon lamp). High yields (63%) of liquids are obtained containing mainly LVG. The proposed chemical model relies on the existence of two concurrent processes: dehydration of cellulose producing anhydrocellulose and giving char + CO, CO_2, H_2O; depolymerisation with formation of LVG giving finally rise to volatiles and char (see also Ref. [52]). Finally, in 1989, Tabatabaie-Raissi et al. [53] report results of pyrolysis kinetics studies, performed in an original system associating a TGA and an image furnace. The Arrhenius parameters of a one way model are calculated in agreement with those obtained at low temperature.

In 1983 and out of the solar (and concentrated radiation) context and from experiments performed in differential scanning calorimetry (DSC), Mok and Antal [54] measure the heat demand in cellulose pyrolysis. The authors propose a new detailed model allowing to explain the pressure and flowrate effects: high pressure as well as low flowrate increase char formation and reduce heat of pyrolysis. The model accounts for the different types of charcoals evidenced according to their morphology and origin (from anhydrocellulose or LVG). The model supposes that primarily formed active cellulose competitively gives anhydrocellulose and LVG. However the authors do not discuss the nature of this intermediate primary product nor its mechanism of formation.

In his thesis, Diebold [45] proposes a cellulose global pyrolysis reaction scheme accounting for the formation of char, primary vapours, secondary gases and secondary tars from an intermediate active state. The feed gives directly a fraction of char and H_2O only in slow pyrolysis conditions.

Following the Diebolds "Hot Wire" observations, Lédé et al. [55] publish in 1985 the results of their "Spinning Disk" experiments. Schematically, a wood rod is applied under known pressures (0.1–3.5 MPa) on a hot disk (773–1173 K) spinning at different velocities. The thickness of the pyrolysis zone (10–100 μm) at the end part of the rod as well as its rate of consumption (a few $\mathrm{m\,s^{-1}}$) are studied as a function of experimental parameters. No noticeable quantities of char are formed. The wood–disk contact appears as if it was lubricated, evidencing the primary formation of a liquid (similar observation as in the "Hot Wire" experiments of Diebold [46]). In 1994, Peacocke [56] confirms similar observations. In 1987, Lédé et al. [57] publishes similar types of "Spinning Disk" experiments performed with true melting materials such as ice, rilsan, paraffine, etc. The corresponding measured values of melting rates lead to the same qualitative behaviours as a function of experimental parameters. From a simple general model, it is concluded that wood behaves as during a fusion, with an estimated melting temperature of 739 K ("Fusion like behavior of wood").

These phenomena have been modelled by Martin et al. [58] who solve Navier–Stokes and energy equations at the interface between a hot plate and a true melting material, with comparison to the case of a fast pyrolysis biomass sample. They show that the ablation velocity is proportional to the fourth root of the applied pressure and inversely proportional to the square root of sample cylinder diameter. A universal relationship is proposed to correlate dimensionless values of ablation rate and applied pressure, and gathering results obtained with true melting materials and fast pyrolysing biomass. All these fundamental experiments and Diebold "Hot Wire" observations are at the origin of the so-called "fast ablative pyrolysis" that basically relies on the primary formation of a liquid phase when biomass, applied on a hot surface, is submitted to high external heat flux densities.

Three other interesting papers are published in 1987.

Evans and Milne [59] use the molecular-beam mass spectrometry (MBMS) technique to the elucidation of the molecular pathways involved in the fast pyrolysis of wood and its main components. On the basis of their results, the authors summarise their observations in a simple diagram valid for any biomass. They distinguish the conditions of high and low pressure pyrolysis. As a function of pyrolysis severity and taking into account primary, secondary and tertiary processes, they classify the products into solid phase (biomass, charcoal directly issued from biomass and retaining its original morphology, coke and soot resulting from secondary reactions), liquid phase (including primary liquids and condensed oils) and vapours phase. In the case of cellulose, the observed products contain a large fraction of LVG, other peaks being fragments ions formed from LVG. On the basis of previous other works, the author rapidly discuss on the existence of active cellulose formation step and corresponding to a decrease in DP form 1000–2000 to 200 at temperatures between 493 and 523 K. Rapid cellulose weight loss begin around 553 K with an inflection point around 573 K, temperature at which transglycosylation process leads to the formation of high LVG yields. All the transformations that could contribute to the rate limiting step are discussed. They underline the strong influence of the presence of inorganic matter. In the general case of wood, the direct production of liquids is postulated to occur mainly at pressures above atmospheric. The authors remind the results of Diebold's direct contact fast pyrolysis experiments where wood exhibits properties similar to those of a molten plastic state, and also of the existence of a glass transition temperature of wood. The direct formation of a liquid product would hence result from the pyrolysis of a "plastic" wood.

Radlein et al. [60] report the results of HPLC analysis of liquids obtained in the Waterloo fast pyrolysis process (fluidised bed operating at 793 K and 1 atm). It is confirmed that the main product is LVG. However, the authors evidence also the formation of a dimer (cellobiosan). It is shown that cellobiosan is not formed through levoglucosan polymerisation but is a cellulose pyrolysis primary product (supporting the theory that cellulose is a polymer of cellobioside units).

Richards [61] evidences the major formation of hydroxyacetaldehyde (HAA) in batch experiments of cellulose pyrolysis performed in vacuum (1 mm Hg) at 623 K. They show that, in these conditions, LVG is not a major product. HAA would be formed concurrently with regard to LVG: the conditions which decrease LVG yields cause a strong increase of HAA yields, as for example with NaCl pretreated cellulose. The authors underline the agreement of these results with those of Piskorz et al. [62] obtained under ambient pressure.

In a 1988 paper, Piskorz et al. [63] study the liquid products obtained from cellulose fast pyrolysis performed in a fluidised bed (Waterloo fast pyrolysis process) at 762–773 K and under gas residence times between 0.46 and 0.50 s. It is shown that liquid yields increase under experiments made with very pure cellulose, whilst LVG increases and HAA decreases. The reverse is observed in the presence of pretreated cellulose. The authors propose a general kinetic model (Waterloo model) including two concurrent reactions. Their relative importances depend on the nature of cellulose (for example its DP), fraction of inorganics, salts and temperature. In the first one (fragmentation, decarboxylation, dehydration) HAA and other low molecular weight oxygenated compounds are the main products. In the second one, LVG is the major product. These two reactions occur from so called "cellulose low DP" that would be rapidly formed from cellulose starting material. However this initiation reaction is not deeply described. To be noticed that charcoal, gas and H_2O can be formed directly from cellulose but only in low temperature and slow pyrolysis conditions.

In 1989, Essig et al. [64] report new results of cellulose pyrolysis obtained under vacuum and between 623 and 773 K. They confirm that the volatile products formation occurs according to 2 dominant concurrent pathways leading either to LVG or to HAA. Their yields increase as the pressure is decreased. The high temperature favours HAA formation. They confirm also that LVG yield strongly increases if inorganics contents have been previously extracted from cellulose. In their discussions, the authors confirm that the first steps in cellulose pyrolysis results in DP reduction without weight loss. The scissions would occur in surface chains of the cellulose crystallites.

In the same year, Pouwels et al. [65] compare the reaction products formed by Avicel microcyrstalline cellulose pyrolysis performed with three pyrolysis methods. In all the cases, the authors show the formation of anhydro oligosaccharides, LVG being not a primary product of reaction. Actually, they confirm that the first step in the thermal degradation is a depolymerisation leading first to anhydro oligosaccharides. They would then subsequently undergo further decomposition leading to lighter species such as LVG. These mechanisms would be relatively independent of parameters such as heating rate and final pyrolysis temperature.

As a conclusion of this period, new experimental direct evidences have been given on the existence of short life time intermediate species. New kinetic models are reported. Most of them include two main processes giving concurrently rise to LVG and HAA. Good agreement exists as for the conditions maximising each of these 2 compounds. However, they do not appear as being the primary products and most of the mechanisms include primary initiation processes of cellulose depolymerisation giving intermediately rise to low DP species.

6. New models and controversial papers published in the 90s

A great number of papers are published during this period. New kinetic schemes are proposed as well as sample particle models taking into account heat and mass transfer phenomena. These papers reveal controversies notably related to the existence and role of short life time intermediate species such as active cellulose.

6.1. Controversial papers

In 1993, Varhegyi et al. [66] scrutinised the results of Mok et al. [67] experiments of crystalline cellulose pyrolysis in sealed crucibles under high pressure. Very high yields of char were obtained. Amongst the different kinetic models used only one could mimic the results. This model involves two primary reactions of cellulose. The first one produces char, volatiles, H_2O and gases (as in TGA at low pressure). The second one produces intermediates giving also rise to char, H_2O and gases. The reactions are shown to be catalysed by water. The model does not take into account an initial step of cellulose depolymerisation.

In a paper entitled "Is the Broido–Shafizadeh model for cellulose pyrolysis true?", Varhegyi et al. [68] seriously question the validity of the BS model. The paper reports TGA experiments of small Avicel cellulose samples pyrolysed under temperatures 523–643 K with prolonged thermal pretreatments. The results confirm the role of two parallel reactions directly issued from cellulose. In the absence of prolonged thermal pretreatment, only one of these reactions is considered. It is a first order irreversible reaction for which an activation energy of 238 kJ mol^{-1} is calculated. The result is that a simple first order model appears to be able to accurately mimic weight loss data at heating rates above 2 K min^{-1}. In their conclusions, the authors claim that under their experimental conditions, the cellulose → active cellulose step in the BS model is superfluous within the temperature range 523–643 K. The char fractions are also much lower than those usually reported in the literature thanks to the very small sample masses (minimisation of vapour–solid interactions).

Other conclusions can be also found in a 1995 review [38] where the same authors discuss the role of inorganics and the major origins of char. The results are mainly related to experiments performed in TGA under heating rates ranging from 1 to 100 K min^{-1}. Amongst the main conclusions of the paper:

- In conditions that minimise the vapour–solid interactions as well as any heat transfer limitation, weight loss in cellulose pyrolysis can be simply represented by a single irreversible first order reaction with a high activation energy of 238 kJ mol^{-1}. To be noticed that this value is quite close to that of the cellulose → active cellulose step in the BS model [39] (Eq. (1)).
- The BS model is not relevant to the design of biomass combustors, gasifiers and flash pyrolysis reactors. However, it can be pointed out that the experimental conditions (TGA) under which have been obtained these results are not quite representative of those encountered in these processes.
- The only source of char result from heterogeneous vapour–solid interactions that are catalysed by water
- The high activation energy associated to strong endothermicity can explain the much lower activation energies reported in the literature.
- Minute amounts of inorganics can considerably modify the pyrolytic behaviour.

In 1995, Milosavljevic and Suuberg [69] publish results obtained in TGA conditions bringing new insights as for the controversies concerning the activation energy of pyrolysis. They report that kinetics are sensitive to the heating rate. In the cases where cellulose is rapidly heated above 600 K a low activation energy is found (140–155 kJ mol^{-1}). Alternatively in conditions of slow heating below 600 K, the activation energy is much higher (218 kJ mol^{-1}). A new model relying on three parallel reactions is proposed. The reaction occurs directly from cellulose without passage through intermediate species. The year after (1996) Milosavljevic et al. [70] study the thermal effects in connection with char formation by DSC and TGA (heating rates 0.1–60 K min^{-1}). In the absence of mass transfer limitations, the main pyrolysis pathway is endothermic (result of primary species vaporisation). In the presence of mass transfer limitations and under low heating rates the process is exothermic with enhancement of char formation. The enthalpy of cellulose pyrolysis thus depends on operating conditions. It is pointed out that pyrolysis would initially follow a common pathway irrespective of heating rate until a finite level of conversion.

In their 1998 review, Antal et al. [71] comment the 1995 results of Milosavljevic and Suuberg [69]. In agreement with their previous papers, the authors confirm that in all their experiments, the pyrolytic weight loss can be represented by a single first order law at both low and high heating rates (activation energy of 228 kJ mol^{-1}). They explain their disagreements with Milosavljevic et al. as resulting from inaccuracies in the temperature measurements with large samples and from mass transfer limitations. The higher the inhomogeneities of temperatures the lower the activation energies.

6.2. New evidences of an initiation step

These last models issued from mass loss measurements do not take into account the existence of active cellulose. During this period, however other papers bring new evidences of the existence of intermediate species. For example, in her 1993 thesis, Vladars-Usas [72] studies the fast thermal decomposition of Avicel cellulose samples (75–212 μm) inside a transport flow reactor under temperatures between 1123 and 1473 K. The residence times are of a few tens of ms. A mathematical model predicts particles reaction temperature of about 823 K. The results clearly evidence that depolymerisation of cellulose occurs through a water soluble molten state. Noticeable fractions of LVG, cellobiosan and anhydrooligosaccharides are found. Their fractions are favoured by high heating rates and short residence times.

Five years later, Boutin et al. [73] report experiments of the behaviour of cellulose powder submitted to high radiant heat flux densities (image furnace operating with a 5 kW xenon lamp associated to two elliptical mirrors). Microscopic observations show that for exposures ranging between 0.2 and 1 s, the powder passes through a liquid yellowish phase leading to further agglomerations. These products are liquid at reaction temperature and solid after rapid cooling. They are soluble in water, showing that they are no more cellulose and that their formation does not correspond to a simple melting but to a partially degradated cellulose. For longer exposure times, these products give rise to condensable vapours as well as a small fraction of gases. Practically no char formation is observed. The authors report also the results of a simple mathematical modelling of the phenomena, relying on the BS model, associated with the kinetic constants given by Bradbury et al. [39] (Eqs. (1)–(3)). The good agreements with experiments confirm, in these fast pyrolysis conditions, the validity of the BS model, which in this case, is reduced to 2 reactions in series (cellulose → liquid intermediate → vapours) because of no char formation. The model confirms that the reaction occurs at a temperature close to 750 K. The life time of the liquid species is much lower than 1 s and their mass fraction can theoretically reach 90%. The same authors [74] will confirm later these results: evidence of liquid formation having life times of a few tens of ms under an available heat flux of 2×10^7 W m^{-2}.

In their paper presented at the meeting "Frontiers of pyrolysis: biomass conversion and polymer recycling" (Breckenridge, CO, June 1995), Piskorz et al. [75] comment several published results, as those of Lédé et al. [57] who described ablative pyrolysis as a "fusion like" phenomenon with a reaction temperature of about

739 K. The authors notice that this temperature is close to that which can be calculated from glass transition temperature measured by Back et al. [16] on the basis of a relationship between fusion and glass transition temperatures and valid for several types of polymers (see above). The calculated fusion temperature for cellulose would be of about 723 K. From kinetic constants calculations, the authors conclude that the activation step in the BS model would, in fact, correspond to a phase transition (melting) rather than a chemical transformation whilst underlining that such a very fast melting is difficult to observe without some pyrolytic decomposition. However, a true melting phenomenon can be questioned as it has been shown that these species are water soluble unlike cellulose. The authors confirm the Waterloo kinetic model [63] which takes into account the passage through low DP species that may decompose according to two competitive reactions.

In experiments performed with very small samples size and/or under low heating rates it can be usually expected that apparent kinetic behaviour is mainly controlled by pyrolysis chemical reactions alone. In the other cases (large samples), other physical phenomena such as heat and mass transfer resistances cannot be ignored as they may control the overall kinetics. Their competition with chemical phenomena needs the solving of mathematical models written at the particle level. After several pioneering works such as those of Villermaux et al. [76], and Pyle and Zarror [77], a great number of models have been published. They are more or less complex according to the level of simplification of the assumptions. We shall mainly consider those related to cellulose and not those made in the general case of biomass (wood).

6.3. Models of cellulose particle pyrolysis

In 1994, Diebold [44] reports the results of a model relying on the chemical mechanism used in his thesis [45]. The fractions of products are calculated as a function of time, temperature, heating rate and pressure in conditions of either slow and fast pyrolysis (heating rates are varied in the range 0.01–60 000 K min^{-1}). The model relies on the assumption of linear increase of particle temperature. Even if such a behaviour cannot be practically reached, the results are interesting and allow to calculate estimates of active cellulose maximum production as function of heating rate. The results confirm that in fast pyrolysis conditions, the primary reaction occurs between 723 and 773 K and that the char fraction is strongly minimised under vacuum operation. Under very high heating rates active cellulose weight fraction may exceed 90%.

Two years later, Miller and Bellan [78] report the results of a detailed mathematical model representing the pyrolysis of porous solid particles. For cellulose, the authors use the BS model. The aim is to estimate the effects of temperature, heating rate, porosity, particle size, etc. . . .on the char yields and conversion times. Three regimes are distinguished: initial heating; primary reaction at the effective pyrolysis temperature (between 600–650 K with only small variations whatever the operating conditions); final heating.

Many works have been published by Di Blasi and her colleagues on biomass pyrolysis. We shall consider only those related to cellulose.

The ablation experiments of Lédé et al. [55] published in 1985 are modelled by Di Blasi [79] in 1996 on the basis of the interface heat transfer coefficient given in Ref. [55]. The BS model is used. The variations of ablation velocity, thickness of reactional zone and products yields observed by Lédé et al. [55] as a function of the hot spinning disk surface temperature and applied pressure, are confirmed. It is verified that the reaction regularly propagates towards the virgin heart of the rod sample with existence of two reactional fronts. The first one is associated to the melting of cellulose and the second one to the vaporisation of melted intermediate species. Very few char fractions are formed.

In the same year, Di Blasi [80] investigates the coupled effects of particle size and external heating conditions on cellulose pyrolysis accounting for all main transport phenomena, variable chemical physical properties, primary and secondary reaction processes. The kinetic scheme relies on the BS model extended to gas production from the tars (cracking reactions). In spite of Antal and Varhegyi conclusions the active cellulose formation step is taken into account because this step is expected to be important, when temperature and particle heating rate are much higher than in TGA. Several reacting regimes are evidenced, from kinetically controlled, to heat transfer controlled situations. The effects of reactor heating rate (0.25 until 15 K s^{-1}), particle size as well as reactor final temperature on tars and char fractions and reaction temperature are studied. The results confirm that sample temperature does not reach the final reactor temperature and is situated between 650 and 750 K. However, no data are given about active cellulose behaviour.

The following year, Di Blasi [81] uses the same extended BS model for studying the influence of several physical properties on devolatilisation characteristics. The reactor imposes a convective and radiative heat flux. The influences are mainly important in the case of large particles with reaction temperatures close to 650 K. Secondary char formation is not taken into account. In the same year, Lanzetta et al. [82] publish results of an experimental investigation on heat transfer limitations in the flash pyrolysis of cellulose. The mass loss of a thin layer of cellulose powder submitted to a radiant heating is measured in conditions minimising secondary reactions. The temperature is measured by a fine thermocouple in contact with the sample. The authors interpret their results on the basis of a modified version of the BS model where the first step of active cellulose formation has been dropped according to Varhegyi et al. [68] conclusions. The authors expect that this process does not seem necessary for predicting global kinetic degradation in chemical regime (and in experimental conditions of mass loss measurements). However the authors point out that a change in physical properties (i.e. melting) can be important in certain practical situations (as in ablative pyrolysis for example).

In 1998, Di Blasi [83] uses the BS model for studying the physicochemical processes occurring inside a degradating anisotropic medium with application to cellulose. 2D and 1D models are compared. In the same year the same author [84] compares several different kinetic schemes on char, tar and gas fractions in conditions of chemical reaction control. The chosen models include those of Broido, BS (with active cellulose) and modified BS models (without active cellulose and on the basis of Varhygyi et al. [85] kinetic constants). The simulations are firstly made under high heating rates (50 K s^{-1}) and final temperatures 550–1000 K, and secondly under slow heating rates (20–160 K min^{-1}) and final temperature of 800 K. All the models give the same qualitative results (tar increase, char and gas decrease as the conditions are more severe). The authors conclude that each one may be a good approximation.

In her modelling of cellulose fast pyrolysis in a fluid bed reactor, Di Blasi [86] takes into account all the processes involved: transport phenomena, fluid bed hydrodynamics and chemical reactions. The BS model extended to secondary reaction (homogeneous cracking) is used. The results (in agreement with literature) show that in the conditions of liquids production maximisation, the mean particles heating rates depend on their sizes and of fluid bed temperature, whilst their actual reaction temperatures vary in a narrow range (600–725 K).

The results of a Round-Robin study of Avicel PH-105 cellulose pyrolysis performed by 8 European Laboratories (heat source heating rate between 5 and 40 K min^{-1}) are published in 1999 by Gronli et al. [87]. The peak temperature and weight loss are in good agreement at 5 K min^{-1} but less good for residual char yields. At 40 K min^{-1} larger scatters are observed mainly due to uncertainties in actual temperature knowledge (“Thermal lag”), a result confirmed by the influence of cellulose mass sample. All the data can be represented according to an irreversible single step and first order rate equation with a high activation energy (244 kJ mol^{-1}) and a pre-exponential factor $\log A = 19$. The possible existence of active cellulose is not mentioned. However it can be noticed that these Arrhenius parameters are quite similar to those determined by Bradbury et al. [39] (Eq. (1)) for the initial active cellulose formation.

7. First detailed discussion in 1999 on the existence or not of an intermediate state in biomass pyrolysis [88,89]

As seen in the previous sections, several kinetic schemes were used by the authors at this date. They included or not the primary formation of intermediate species (like active cellulose). Even if their existence had been evidenced long before, another question raised about the need to take into account these species in the models. In a paper entitled "The nature and properties of intermediate and unvaporised biomass pyrolysis materials" presented at the Banff meeting, Lédé et al. [88,89] gather and discuss a great number of experimental and theoretical results. Two main kinetic schemes are compared: the BS model (with Bradbury et al. [39] kinetic constants (Eqs. (1)–(3)) and the simple one step model proposed by Antal and Varhegyi [28]. Fast and slow pyrolysis are both considered. Following are the main discussions and conclusions reported at the date of the paper (1999).

7.1. Actual reaction temperature

In fast pyrolysis conditions, this worldwide used important parameter (as well as actual sample heating rate) is very difficult to experimentally measure for several reasons. The chemical processes and life time of intermediates are very fast/short. The measurements are very difficult with small moving particles whilst in the case of big samples important internal gradients exist. Strong interactions may exist between thermocouple and outside source of heat with also contact resistances, etc. [90–93]. Conversely, in slow pyrolysis (ex. usual TGA) the values are usually reliable under conditions of low heating rates. So, except in this case, actual reaction temperature can only be estimated through modelling of the sample pyrolysis. In fast pyrolysis, and because of the endothermic nature of the reactions, the sample actual temperature is usually much lower than that of the heat source with only small variations according to operating conditions. Such a phenomenon is at the basis of so-called "fusion like" behaviour of the solid pyrolysis. From Bradbury et al. [39] kinetic constants this temperature would be around 750 K for cellulose. A consequence is that cellulose can hardly be heated above this domain of temperatures without previous decomposition. Consequently the validity of primary kinetic constants measured at expected very high temperatures can be questioned.

7.2. Physical nature of the primary products

In Lédé et al.'s "Spinning Disk" [55] and Diebold's "Hot Wire" [46] experiments, the friction of biomass against the hot metallic surface gives the feeling of smooth lubrication. This is the result of the presence of a fluid at the biomass–hot walls interface. Is that fluid a liquid or a gas? In these experiments, the sliding resistance increases as the wall temperature decreases (increase of fluid viscosity). No lubrication effect is felt with wall temperatures close to those usually explored in TGA. In the spinning disk experiments, a visible tail is left on the disk, which rapidly disappears into vapourish products. Char is left of the disk only at low walls temperatures showing that such char would be directly formed from the liquid (tail) in competition with vapours formations. Thus, secondary vapour–solid mechanisms do not seem to be the main source of char in these conditions.

An estimate of the velocity of radically escaping fluids ("Spinning Disk" experiments) has been calculated from a very simple mass balance written at the biomass–hot walls interface. In the assumption of a vapourish nature, such a velocity would be of the order of 10^4 m s^{-1} (much higher than sound velocity!) which is quite unrealistic. Another simple calculation shows that the fluid viscosity would be roughly 1000 times higher than that of a gas at 740 K.

All these results show that in conditions of fast ablative pyrolysis, the primary fluid products are under the form of a liquid rather than of a gas, bringing arguments in favour of the BS type model.

7.3. Chemical kinetics considerations

The determination of kinetic constants is a very difficult task. They often result from experiments performed in TGA in conditions (low heat source temperature increasing with time, with very small particle masses, etc.) which are quite different from those encountered in actual reactors. Unfortunately, even in these cases, there are difficulties in the determination of actual sample temperature [90]. On the other hands, models show that in most of actual fast pyrolysis reactors (operating often with fixed heat source temperature [3,4,91–93]), the actual temperature reached by the reacting samples are higher than in TGA and thus, the controlling chemical processes may be different (if several elementary processes with different activation energies are involved).

Assuming the validity of Bradbury et al. [39] (Eqs. (1)–(3)) kinetic constants (indeed obtained at low temperature but under vacuum, hence minimising mass transfer problems) the k(vapours)/k(char) ratio greatly exceeds 10 above 723 K confirming that volatiles are favoured at high temperature. In these conditions the k(active cellulose)/k(vapours) ratio is much greater than 1 meaning that the step giving rise to vapours would be rate limiting in fast pyrolysis conditions, and so, active intermediate would be produced (from the feedstock) in high yields before its further conversion. So, in conditions of TGA, this step could not be easily observed and one step mechanisms would be sufficient. However, Bradbury et al. [39] have measured their primary pyrolysis kinetic constants under very low temperatures (532–568 K) where the k(active cellulose)/k(vapours) ratio is close to 4 showing that the initial step of active cellulose formation would be more rate limiting than at high temperatures. It can be concluded that intermediate active species would be also formed under very low temperatures but in very low concentrations. So it could be anticipated that these species could be observed in low concentration in TGA providing that the sample is maintained a longer time at these low temperatures. In these conditions, active intermediate could be assumed to be close to a high viscosity liquid or more likely a very little deformable plastic material rather than a true liquid. Such a property would explain that in these low temperatures pyrolysis conditions, char formed from active intermediate apparently keeps the initial structure of the feedstock whilst in fast pyrolysis, char clearly results from being issued from a liquid.

The paper shows also that the kinetic constants derived from cellulose experiments are quite predictive for wood itself.

7.4. Chemical structure of the primary products

At the date (1999) of this paper, it was difficult to conclude if the active intermediate was or not a short life time melted form of cellulose. Such an assumption could be partially excluded as it had been shown that active cellulose was water soluble unlike cellulose. Another question was whether the volatiles were formed according to a simple boiling phenomenon from the active. Very rough calculations showed that the boiling points would be 612 K for LVG, 854 K for cellobiosan and 1065 K for the trimer. These values suggest that in TGA (mass loss occuring between roughly 573 and 623 K), LVG would rapidly vaporise whilst the other oligomers would not be very volatiles. In fast pyrolysis conditions, the volatiles would be also mainly made of LVG suggesting that active would be made of oligomers undergoing cracking inside the liquid phase. Such an assumption was supported by the results of Pouwels et al. [65]. The presence of higher oligomers in the oils recovered after vapours condensation could result from further recondensations of monomers or through other processes such as the trapping of aerosols escaping directly from the reacting sample.

8. Last decade (2000 until now): new results, new models, new evidences for the existence of primary intermediate species

In 2000, confirming the results of Vladars-Usars [72], Piskorz et al. [94] publish the results of fast pyrolysis experiments carried out with Avicel cellulose in a downflow tubular reactor. A mathematical model is also reported. The reaction temperature is confirmed to level between 773 and 823 K (even for much higher heat source temperatures). From the recovery of solids residues, up to 44% of a water soluble fraction is obtained. Significant yields of LVG and only anhydrosaccharides with degrees of polymerisation ranging from 2 to 7 are analysed as well as non-identified material with DP > 7. Photographs confirm the liquid nature of primary products.

In 2001, Banyasz et al. [95] study the gas evolution and mechanisms of cellulose pyrolysis performed in conditions of rapid temperature increase from 653 to 1023 K within about 1 min. The time evolution of formaldehyde, HAA, CO and CO_2 are studied in a fast evolved gas FTIR apparatus. The three first products fractions increase with heating rate whilst CO_2 decreases. The proposed kinetic scheme states that initial cellulose decomposes according to two competing reactions giving anhydrocellulose leading to char 1, and a depolymerising process (with formation of active cellulose). Active cellulose (and char 1) is, in turn, expected to decompose into two other competing reactions: one going rise to tar + CO_2 + char 2 and the other one giving intermediates that can decompose into HAA or (fast) formaldehyde + CO. The corresponding activation energies are measured. The tars contain mainly LVG, confirming the well-established competition between LVG and HAA formation, the second one being favoured at high temperatures. Finally the authors compare their model to that of the BS model. Except for charring these two models lead to the same results in terms of weight losses.

The results of cellulose pellets fast pyrolysis are published in 2002 by Boutin et al. [96]. The experiments are performed under controlled flash times (lower than 1 s) of a concentrated radiation provided by an image furnace under very clean conditions of imposed flux densities (varied between a few 10^5 and 7.4×10^6 W m^{-2}). The pellets are settled inside a transparent quartz reactor fed by an inert gas at room temperature with quenching of the primary pyrolysis species. All the products are recovered and mass balances are close to 100%. After each flash, eye and microscopic observations of the sample reveal the existence of two distinct surimposed layers. At the back side, a layer of unreacted fibrillar cellulose and at the front side, a yellow layer made of networks of agglomerated melted particles. This yellow material is solid at room temperature and soluble in water. It has been called “Intermediate Liquid Compound (ILC)” by the authors. Under high flux densities no char is formed. However under about 9×10^5 W m^{-2} [97] the ILC layer (at the front side) covers by a third black layer. Its microscopic observation shows to be formed from the solidification of a liquid medium. A complete modelling of the phenomena taking into account heat transfer resistances has been made in the case of high flux densities. Chemical reactions rely on the BS model from which char formation reaction has been removed. Kinetic constants are those of Bradbury et al. [39] (Eqs. (1) and (2)). Results show very good agreement with experiments showing that these kinetic constants determined at low temperature for cellulose are also valid in fast pyrolysis. ILC layer thickness is estimated between 100–200 μm and its life time of the order of 20 ms. The model confirms also that the ILC thickness reaches a steady state value after an initiation period. The steady state cellulose–ILC interface temperature is calculated to be 716 K (close to the “fusion like temperature” previously published [55,57,88] whilst the ILC surface exposed to the radiation (front side) would be near 947 K (estimate of ILC vaporisation temperature).

The natures of products obtained in these conditions (and under absorbed flux densities ranging from 2×10^5 to 4×10^6 W m^{-2}) are reported the same year by Lédé et al. [98]. The gas composition (GC analysis) does not reveal detectable fractions of CO_2. The main gases are CO, H_2 and light hydrocarbons. The molar fractions of these C1 and C2 hydrocarbons are considerably higher under conditions of char formation (lower flux densities) whilst other gases are not significantly changed. The ILC and condensed vapours chemical compositions are determined by HPLC and HPLC/MS analysis. Only anhydrooligosaccharides are detected. For ILC, high DP species (until steptoasan) are in a great majority, whilst the fractions of cellobiosan (around 11%) and LVG (around 5%) are of minor importances. These fractions do not significantly vary with the flash time. The vapours condensed downstream of the quartz reactor contain much higher fractions of cellobiosan and LVG, but always noticeable fractions of higher DP species (3–7). They respectively increase and decrease with the flash time. These results show that unlike many other published results, LVG is not the main primary product. Higher DP species would be produced prior to LVG. Several explanations are given accounting for the presence of high DP in the condensed vapours (in spite of their high expected boiling points) and also the non-negligible fractions of permanent gases in spite of the efficient quenching in the reactor [98]. HAA has never been observed in these experiments.

Contact as well as radiant ablative pyrolysis of biomass occur through the passage through ILC. However, in similar available heat flux densities conditions, Lédé [99] shows that different ILC behaviours can be observed because of different mass transfer efficiencies and residence times at high temperature. Some of these conclusions can be also found in another recent paper [4].

Results of cellulose fast pyrolysis performed inside a heated reactor are reported in 2004 by Luo et al. [100]. The fractions of char, gases and condensed vapours (analysed by GG and GC/MS) are analysed as a function of reactor’s walls temperature and carrier gas residence time. Concerning the condensed vapours, the results show that the production rates and fractions of HAA and 1-hydroxy-2-propanone increase with temperature in the case of short residence times. This reaction competes with LVG formation, both being issued from active cellulose. However, its presence is only postulated but not evidenced. From their results, the authors propose a modified BS model where cellulose gives primarily rise to active cellulose which subsequently decomposes according to three concurrent reactions. The results of a simulation relying on kinetic constants given by Bradbury et al. [39], Varhegyi et al. [85], Banyasz et al. [95] and Shin et al. [101] agree with experiments and lead to a rather stabilised reaction temperature slightly above 673 K for a heat source temperature of 883 K.

In the same year, Wooten et al. [102] report results of Avicel cellulose samples pyrolysed inside a ceramic boat settled inside a furnace in the low temperature range 573–598 K. The sample is heated under reaction times ranging from 5 to 210 min.

After cooling, the residue is analysed by ^{13}C cross-polarisation magic-angle spinning (CPMAS) NMR spectroscopy. By successive spectral substraction of the 573 K pyrolysis char, three main carbohydrate components are evidenced: unreacted crystalline cellulose starting material, intermediate cellulose (IC) that resembles a low DP amorphous cellulose and a disordered final carbohydrate (FC). After 30 min heating, FC is the only remaining carbohydrate component. IC is a precursor to both aliphatic and aromatic groups in the char. A significant early weight loss is attributed to the formation of volatiles directly from cellulose. IC which appears as a reaction intermediate disappears rapidly for temperatures higher than 573 K. IC which is likely composed of oligosaccharides (including anhydro glucose oligomers) is associated to active cellulose. According to the authors, it appears as corresponding to the ILC observed by Lédé et al. [96,98] in fast pyrolysis conditions. These results show that such intermediate species usually evidenced in fast pyrolysis conditions are also formed in the low temperature domains. The role of inorganics is also discussed. From all these observations the authors propose a new low temperature model of low temperature cellulose pyrolysis.

The “Melting of Cellulose” is studied by Schoeter and Felix [103] in 2005. In their introduction, the authors cite several papers reporting that cellulose does not melt and other ones evidencing the passage through a liquid phase. The basic idea of the work is to show, if by means of rapid heating, cellulose thermal degradation can be prevented before melting. Cellulose samples are plastically deformed by the use of mechanical shear, uniaxial pressure and laser radiation. The resulting compact transparent disks are examined by IR spectroscopy and microscopy. The IR spectra do not reveal differences before and after the treatment, meaning that cellulose would not have been chemically modified, leading the authors to claim that they managed to melt cellulose. However they recommend further studies of the DP and crystalline structure of the produced material. As an application of the process, the authors suggest the conversion of cellulose into plastic products (fibres, films). To be noticed that Piskorz et al. [94] suggested the preparation of sugars from active cellulose prepared by fast pyrolysis.

Investigations on the kinetics of the thermal decomposition of crystalline cellulose in wood by in situ X-ray diffraction using synchrotron radiation has been made by Zickler et al. [104]. The fibre diffraction patterns are studied as a function of heat treatment time (a few min until a few hours) under temperatures ranging from 573 to 633 K. Heating is performed by the use of a furnace relying on the use of halogen lamps and elliptical mirrors. The results show a thermally activated reduction of the microfibril diameters with random breaking of the fibres into shorter species due to anisotropic nature of the material.

In the framework of a theoretical study on biomass pyrolysis kinetics, Ranzi et al. [105] consider the great number of elementary chemical and physical phenomena that occur inside a reactor (transfer resistances, solid and gas phase reactions, etc.). The reactions of the three main biomass components (cellulose, hemicellulose and lignin) are taken into account. The multistep lumped mechanisms used for cellulose includes the intermediate formation of active cellulose, even if a small fraction (maximum 5%) of char (+H_2O) can be formed directly from cellulose. Active cellulose decomposes according to two competitive processes giving respectively rise to LVG (mainly at low temperature) and to decomposition products (including HAA, glyoxal, etc.), which become significant at temperatures higher than 723–773 K. Kinetic coefficients as well as kinetic constants are mainly taken from TGA experiments previously published. To be noticed that the selected activation energy for the primary processes of active cellulose formation (192 kJ mol^{-1}) as well as pre-exponential factors (4×10^{13} s^{-1}) are much lower than the values reported by Bradbury et al. [39] (Eq. (1)) which are usually adopted in the literature.

In 2008 Liu et al. [106] publish a paper related to the mechanisms of formation and evolution of active cellulose during cellulose pyrolysis. The experimental set up based on the use of an image furnace (elliptical mirror and xenon lamp) is similar to the one designed by Boutin et al. [96] and Authier et al. [107]. Values of cellulose reflectivity determined by Boutin et al. [96] are used to calculate the absorbed flux as well as an estimate of heating rate. Simple observations confirm the formation of a yellowish layer (colour intensity depends on flash time) on the surface of the irradiated sample. These products are analysed by HPLC. Their chemical composition depends on the flash times and heat fluxes. For small flash times (0.09 s under high heat fluxes), a peak of polysaccharides with an average DP of 14 is clearly evidenced, with formation of methylglyoxal. As the time is increased (until 0.53 s), other products are analysed (cellobiose, glucose and LVG). The progression rate of this sequence is slower under lower heat fluxes. On the basis of several other observations, the authors propose an improved new mechanism explaining the evolution of the different species. The mechanism includes the direct and fast formation of low DP (14) cellulose followed by two concurrent reactions. The first one (fragmentation) gives directly rise to methylglyoxal. The second one (depolymerisation) leads to active cellulose formation (containing cellobiose, cellotriose, . . ., glucose, fructose) giving rise to further consecutive reactions with formation of LVG, char and gases.

On the basis of a literature review and of theoretical considerations, Mamleev et al. [108] bring interesting new interpretations of the phenomena. It is claimed that, neither dehydration nor other elimination reactions seem to occur inside the solid polymer cellulose matrix, hence excluding the formation of dehydrocellulose directly from the solid. The involvement of acid–base catalysis in the process is demonstrated. The authors assume the formation of encapsulated and growing cavities containing high boiling temperature tars (LVG) arising as a result of transglycosylation and playing the role of an electrolyte. Volatile acids dissolved in the tars accelerate various heterolytic reactions. Chains ends located at the cellulose–tar interface migrate into the tars. A two levels model for cellulose degradation valid in usual TGA conditions is proposed. It mainly includes two competing reactions occurring directly from cellulose: β elimination and transglycosylation. The latter has a lower activation energy and leads to LVG, cellobiosan, etc. The model includes feedback processes and continuous initiation. It explains why gas formation is a high temperature step. Both main competing reactions are the source of two types of chars. The model is then compared to the BS and Mok and Antal [54] models. This new model does not include the formation of ILC in conditions of existence of an equilibrium between ILC formation and volatilisation, and when only mass loss is considered. However, the authors underline the fact that the problems connected with ILC (as well as its secondary depolymerisation into LVG) remains almost unexplored. They finally recommend to build further theory describing the phenomena occurring at the cellulose–ILC interface.

In the framekwork of a study on the formation of polyaromatic hydrocarbons and dioxine during biomass pyrolysis, Garcia-Perez [109] publishes in 2008 a literature review on the numerous reactions involved in pyrolysis. In the case of cellulose, the author proposes a model summarising several informations collected in the literature. The model includes several types of reactions: low temperature dehydration and depolymerisation (slow pyrolysis and torrefaction); depolymerisation reaction at high heating rates (fast pyrolysis); fragmentation or open ring reactions catalysed by inorganic salts; acid catalysed dehydration reactions; polymerisation of anhydrosugars; cross-linking reactions of fragmentation products; evolution of polyaromatics from char. All these reactions (slow pyrolysis dehydration, alkali cation inhibitied depolymerisation and fragmentation) occur after the initial decomposition of cellulose into low DP species (active cellulose).

In 2009, Dauenhauer et al. [110] report convincing proofs of the passage through a liquid phase during cellulose pyrolysis. The impingement of microcrystalline particles (around 300 μm) onto a heated catalytic surface (973–1073 K) is observed by high speed photography. The production of a liquid intermediate boiling into vapours is clearly evidenced. The droplets appear to be in close contact with the surface (high heat transfer rates) with possibilities of coalescences. After total vaporisation, no char is left on the surface. In other types of experiments (close to ablative pyroysis experiments [55]), rods of cellulose are pressed onto a catalytic hot surface (possibilities of continuous processing). The observations are in agreement with those of Lédé et al. [98]. All the results confirm the passage through an intermediate liquid phase under conditions of high heat source temperature and external available heat flux densities. However, no result related to the DP and/or chemical composition of the liquids is reported, preventing to conclude if these liquids correspond or not to a true melting phenomenon.

In the continuity of these works, Teixeira et al. [111] report experiments (high speed photography) and modelling (CFD calculations) of the ejection mechanisms of aerosols, from thermally decomposing cellulose. The results support a mechanism of interfacial gas bubble collapse forming a liquid jet which subsequently fragments to form ejected aerosols. The liquid intermediate formed from cellulose pyrolysis is called “molten cellulose”. On the basis of literature, it is assumed that it actually contains levoglucosan, cellobiosan, cellotriosan and longer anhydro oligomers. The model supposes that the aerosols result from two possible pathways: evaporation of molten cellulose followed by nucleation/condensation, and also direct ejection of liquids (capable of transporting non-volatile materials: high molecular mass species and also inorganics). Surface tension and viscosity ranges are estimated for molten cellulose. The aerosol particles velocity is estimated between 0.1 and 0.5 m s^{-1}.

9. Discussions and conclusions

9.1. Kinetic models of cellulose pyrolysis

- In spite of the very great number of works published since more than 100 years, no consensus is, nowadays, reached in the literature.
- The simplest lumped models simply rely on the basis of gases, liquids (condensed vapours) and solids (char) phases. Each one can result from several levels of subsequent (primary, secondary, tertiary) transformations. Mechanistic models including radical and/or ionic reactions are, now, more and more often reported.
- Many models are issued from results obtained under low temperature and small heating rates conditions (the reactions are slower and temperatures easier to measure), and often on the basis of mass loss measurements. These experimental conditions are quite different from those prevailing in the actual cases of reactions operating with a fixed heat source temperature (continuous reactors). In the case of fast pyrolysis, the reactions occur also at higher temperatures. They are much faster and low heating rate mass loss results do not necessarily apply. In fast pyrolysis, it is often necessary to pass through the solving of mathematical models implying assumptions of several badly known physical constants.
- A very large range of complexities are considered: from single one step kinetic models until very complex ones including subsequent reactions occurring in the gas and liquid phases or resulting from fluid–solid interactions. Most of reactions include dehydration, fragmentation and depolymerisation processes.
- Unfortunately, some kinetic models are only valid under the well-defined experimental pyrolysis conditions from which they have been derived. Several authors have tried to gather various results obtained in large conditions ranging from slow until fast pyrolysis.
- Cellulose pretreatments influence the results. The concentration and nature of inorganic species have strong impacts on products properties and yields.
- As soon as the 19th century, LVG has been reported as being one of the main final product. Its formation occurs in competition with HAA. It seems now well established that LVG is not a primary product.
- The literature shows the existence of controversies and uncertainties as for the inclusion or not, in the models, of primary intermediate species. According to the authors, the early stages of reactions occur through these intermediate species or directly from cellulose. Many authors include this step in their models but without clear justification. The BS model which has been the first one to include the formation of active cellulose continues to be often cited in the literature.
- Unfortunately, the same word active cellulose is used by several authors for designing the intermediate species obtained in very different conditions (slow and fast pyrolysis, low and high temperature, etc.). These species are obviously of different physical and chemical natures. Other words are also used such as “cellulose low DP”, “Intermediate Liquid Compound (ILC)”, “Intermediate Cellulose (IC)” and “molten cellulose” (MC). IC is suggested to be close to ILC even they have been obtained under very different temperatures. ILC and MC could be expected to be of similar natures. These species are not always liquids according to conditions, etc. It is hence difficult to select only one word for designing all these different primary products. In the following discussion, and for sake of simplicity, we shall use only one word: intermediate active cellulose (IAC), for representing all these types of intermediates.

9.2. Discussions about IAC

9.2.1. Phase change phenomena

The literature brings several evidences of phase changes phenomena during cellulose heating. As soon as the 60s softing has been evidenced (around 510 K and under mild heating) before significant weight loss. A liquid formation has been also observed by several authors (for cellulose and wood itself) under fast heating conditions (radiant heating, ablative pyrolysis, laser radiation, cellulose impinging on a hot surface, etc.). Conversely to usual condensed pyrolysis vapours (bio oils), this liquid is solid at room temperature. It is water soluble showing that it is no more cellulose. It has been shown to be formed at the amorphous–crystalline junctions. Under slow and fast pyrolysis conditions, IAC would be respectively formed in the range 520–750 K.

9.2.2. DP decrease (slow heating)

Under mild heating conditions, cellulose first decomposes into lower DP species (average values decreasing from about 2000 down to about 200–300) before noticeable weight loss. In these conditions IAC life times may be as high as minutes to hours. It has been postulated that this phenomenon could be at the origin of cellulose macromolecules activation [39]. These DP are average values. Actually these species are a mixture of molecules with large molecular weight distributions [35] depending on several experimental factors. It has been reported [103] that intermediate species observed under low temperature (573 K) were surprisingly similar to those (DP < 7) identified under fast heating [96,98]. In these mild conditions, IAC is probably not a true liquid but more likely resembles a high viscosity type material. This could explain why the initial cellulose structure is kept in the char recovered after reaction.

9.2.3. *DP decrease (fast heating)*

In fast heating conditions, the intermediate formation of a liquid has been clearly identified. Its composition depends on the experimental conditions but always contains large fractions of anhydrosugars. It has been shown [96,98] that LVG and cellobiosan are minority and that species having DP ranging from 3 to 7 may represent more than 84%. At the reaction temperature, this IAC life time is of the order of a few tens of ms. Similar qualitative trends are reported by Piskorz et al. [94] for the composition of the water soluble solid products (composition depends also on residence time). In similar experimental conditions as those of Boutin et al. [96,98], Liu et al. [106] evidences the presence of DP = 14 species before IAC formation. Additional components as those identified by Boutin et al. are also analysed. The formation of primary liquid species in fast high temperature conditions explains why char does not keep the initial structure of cellulose. Actually char microscopic photographs reveal a smooth surface pierced with small circular holes [112–114]. This observation evidences that solidification occurs from an ex-liquid state through which vapours (and gases) have passed (same appearance as that of a solidified volcano lava).

9.2.4. *IAC properties*

If the formation of IAC is clearly evidenced, its physicochemical nature differs according to the experimental conditions (temperature, slow/fast pyrolysis, residence time, etc.). It means that there is not a simple type of IAC. Actually various types of IAC having various compositions and properties should be considered. However several questions deserve to be raised:

- At low temperature, are the average DP 200–300 species directly transformed into final volatiles or do they previously pass through the intermediate of lower DP before mass loss?
- At high temperature, are the species with DP lower than about 7 directly formed from cellulose or have they previously passed through higher DP intermediate formation?
- These intermediate species are evidenced from the analysis of samples recovered after the end of a pyrolysis experiment. However, and mainly in the cases of low temperature conditions, the authors do not mention how have been cooled down the samples. If quenching is not fast enough, possible repolymerisation of low DP primary species could not be excluded [44].

9.2.5. *Cellulose melting?*

In spite of all these results, the literature reveals another unresolved question: is the cellulose behaviour, at the first moments of pyrolysis, similar to a simple melting phenomenon (several papers speak of fusion, melting, molten cellulose, etc. [75,103,110,111])? The answer seems to be no:

- The different identified types of IAC have always lower DP than those of initial cellulose.
- IAC is often soluble in water, conversely to cellulose.
- No author reports that it is possible to re-form cellulose after IAC cooling!
- Of course, under extremely fast heating conditions (preventing possibility of chemical reactions), true melting could not be theoretically excluded [103].
- However, if true melting seems unlikely, it is well agreed that phase change phenomena occur during the reaction, producing several types of intermediate structures: from high viscosity plastic material until liquids, depending on reaction temperature. Such a phase change cannot be disputed for cellulose. Actually, it is already well known for lignin, hemicellulose and wood itself [112,113]. By the way, such a behaviour is also well known for coal and polymeric plastics. Experimental and kinetic studies made with these materials could be evidently interesting sources of inspirations for cellulose studies [115].

9.2.6. *Practical interests of IAC*

A best knowledge of physicochemical properties of IAC could have several practical interests:

- Accurate solving of models written at the pyrolysis biomass particle level.
- IAC could be a source of chemicals [94] or of polymeric materials [103] or of different types of chars (from a solid compact state until a porous structure respectively in fast and slow pyrolysis conditions), etc.
- The phase change phenomena may influence the high temperature behaviour of the feedstock particle (for example by modifying internal mass transfer phenomena). It should be also taken into account in reactor design for several reasons.

The existence of a liquid phase at the particle–hot surface interface is of course at the basis of ablative pyrolysis. The properties and maximum recovery of the condensable fractions (bio oil) depend on the life time of the thin IAC interface layer. This life time depends on the competitions between the rate of IAC formation (feedstock depolymerisation), its rate of volatilisation (vapours formation) and its viscosity at the reaction temperature.

In the case of other types of high temperature gas/solid reactors, several phenomena can occur if the process is conducted with moving feedstock particles. A phase change phenomenon can cause particles stickings as they collide. If the mean free path time of the particles is shorter than IAC vaporisation time, agglomerations can occur. Also in hot walls reactors, particles may either bounce or stick on the walls according to their nature and temperature. The plastic or liquid layer formed on the walls can, in turn trap other uncoming particles. If temperatures conditions are such that char can be formed concurrently with vaporisation, these phenomena can finally cause blockings in the reactor.

It has been recently shown [111] that surface tension and viscosity of IAC are important factors in the alibility of IAC to give rise to aerosols formation.

- Very few is known as for the IAC physical properties because of experimental difficulties resulting from its short life time (fast pyrolysis conditions) and from the need of a very efficient quenching for its recovery out of the reactor. These measurements should be ideally made in situ, under reaction conditions (temperature). It is of course particularly true for IAC viscosity measurements. Other unknown IAC properties include thermal conductivity, density, heat capacity, optical properties, etc. . . .for which, literature brings only rough estimates.

9.2.7. *Chemical kinetics connected to IAC*

Likewise, very few is known on the chemical kinetics of both IAC formation and IAC subsequent reactions.

- Depending on the conditions, the related published kinetic models assume either that the whole cellulose sample first depolymerises into IAC giving subsequent secondary reactions, or that IAC is formed in concurrence with direct production of either volatiles or of char, etc.
- The activation energy of the initiation reaction (formation of average DP in the range 200–300) has been calculated by Chatterjee and Conrad [31] to be 227 $\mathrm{kJ\,mol^{-1}}$ (543–583 K). Quite independently Bradbury et al. [39] calculated a value of

242 kJ mol^{-1} (532–568 K) for the formation of IAC. High values (200–250 kJ mol^{-1}) are also proposed by Mamleev et al. [108] at low temperature for tar and gas formation even if the authors do not include IAC in their model. To be noticed that, in their Round-Robin study (TGA experiments), Gronli et al. [87] propose a simple one step model (cellulose gives directly rise to vapours). The corresponding activation energies range between 228 and 244 kJ mol^{-1}. These large values (similar to those reported for IAC formation) can result from the fact that in these conditions, IAC formation, even if not observed, would be rate limiting. In their modelling of cellulose fast pyrolysis, Boutin et al. [97,99] used Bradbury et al.'s [39] kinetic constants (Eqs. (1)–(3)) and found a very good agreement with the experimental IAC concentration. This result suggests that same kinetic constants could be used for representing initial cellulose depolymerisation in both slow and fast pyrolysis conditions. Such a result would merit to be confirmed. All these high activation energies values are representative of unimolecular decompositions.

- The levelling-off of average DP and of IAC fractions vs pyrolysis time is often observed [30,96,98,102,106,108]. It likely results from an equilibrium between cellulose depolimerisation and IAC subsequent reactions. It has been shown [88] that at low temperatures the IAC formation is rate limiting whilst at high temperature (and in fast pyrolysis conditions), its subsequent reactions are clearly rate limiting. The result is that at low temperature, IAC is relatively stable but would be present in low concentration, whilst at high temperature, and in steady state, high fractions could be obtained, however in conditions where IAC has a very short life time.

9.3. *Few recommended basic research topics and related difficulties*

Basic research is necessary and highly recommended in several fields. However as underlined, many experimental difficulties exist. They depend on pyrolysis conditions.

- Kinetic measurements of IAC formation.

  Under low temperature, these reactions are likely rate limiting; IAC life time is long (minutes to hours); actual reaction temperatures and heating rates can be known with good accuracies. However, in steady state, the IAC quantities are low because of secondary faster reactions.

  Under high temperature, overall kinetics may be controlled by secondary reactions and so, IAC concentrations may be high. However, IAC life time is very short (a few tens of ms). It is very difficult to experimentally measure the actual temperature and heating rate at the sample level (actually they can be very different (much lower) than those of the heat source [3,4,92,93]. In addition, the reaction temperatures vary inside narrow domains whatever experimental conditions (fast pyrolysis) bringing difficulties in the accurate determination of Arrhenius parameters.

  Is it licit to consider that the activation energies (IAC formation) are similar at low and high temperatures? Instead of considering a single value of activation energy, would it be advisable to consider activation energies distributions according to the distributions of DP, temperature, etc.?
- Kinetic measurements of IAC subsequent reactions.

  They should be ideally performed in situ in conditions where IAC is produced. This is a very difficult task with small particles. It is easier with large samples where controlling internal heat transfer resistances occur. Actually, the space temperature and reaction rate distributions inside the sample may be connected to time distributions. In this case, initial transitory (first IAC formation when the sample begins to react) and steady state phenomena (levelling-off of IAC formation resulting from an equilibrium between its formation and decomposition, with a moving reacting front) should be considered. However, mathematical modelling (with assumptions of badly known physical properties of IAC – see above) is needed in order to derive kinetic constants.

  Ideally it would be advisable to perform the measurements directly with isolated IAC. However, efficient quenching is needed for its recovery as it is formed. In addition, IAC should be very rapidly reheated until expected reaction temperature (in order to minimise intermediate temperature reactions).
- The role of inorganics has to be clarified. Do they influence the IAC formation reactions (as can be seen for example after cellulose pretreatments, such as impregnation, demineralisation, etc.) or/and the subsequent reactions underwent by IAC [113]?
- Very few data are available as for the enthalpies of these elementary reactions.
- Under high temperatures, low viscosity liquid IAC can migrate through the pores of the sample. IAC-solid sample interactions can occur resulting in secondary reactions (crackings reactions, char formation, etc.). These phenomena are still badly known.
- Mainly in conditions of fast reactions (fast pyrolysis) the liquids which are rapidly formed inside the sample can be violently ejected and form high molecular weight aerosols that can lower the bio oils qualities [88]. These liquid aerosols can also transport non-volatile organic material and also inorganics [111,116]. In depth, experimental and theoretical studies are hence recommended on the role of IAC in aerosols formation (mainly in the case of biomass itself because of the roles of lignin and hemicellulose).
- New concepts of laboratory devices should be imagined for the measurements of IAC physical properties and chemical composition in the case of fast pyrolysis conditions (fast reactions, short life times, etc.). Actually, the measurements would seem easier in TGA conditions. However, the results can hardly be used in the case of fast pyrolysis (probable different types of IAC). In any case, in situ analysis is recommended.
- Similar physicochemical properties measurements are also needed with the other biomass components (lignin, hemicellulose). They also undergo phase changes phenomena, which occur at different temperatures. Combinations of these properties are basic informations for understanding (and modelling) biomass pyrolysis itself [111]. "Fusion like" behaviour of biomass partially depends on the influence of each of its components and of their interactions. Finally, comparison with the similar behaviours of coal and polymeric plastics is highly recommended.

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Glossary

BS: Broido–Shafizadeh
DP: degree of polymerisation
DSC: differential scanning calorimetry
DTA: differential thermal analysis
FC: final carbohydrate
FTIR: Fourier transform infrared spectroscopy
GC: gas chromatography
HAA: hydroxyacetaldehyde
HHV: higher heating value
HPLC: high performance liquid chromatography
IAC: intermediate active cellulose
IC: intermediate cellulose
ILC: intermediate liquid compound
IR: infrared
LVG: levoglucosan
MBMS: molecular beam mass spectrometry
MC: molten cellulose
MS: mass spectrometry
MTA: mass spectrometric thermal analysis
TGA: thermo gravimetric analysis